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TRACE SPECIES EMISSIONS FOR IGFC

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Schedule of Milestones FY 1994 Program Schedule

	S	O	N	D	J	F	M	A	M	J	J	A
Thermodynamic Analysis	██████████											
Gasification Testing	████████████████████											
TGA-Runs	██											
Trace Element Capture Tests											████████████████████	

OBJECTIVES

The objectives of this investigation are to study both the fate and distribution of at least five significant, coal-derived "trace" elements commonly present in coal-gas, in terms of their vaporization during gasification, their condensation and sorption during hot-gas cleanup, as well as their effects on fuel cells, gas turbines, and ultimately the environment. The definition here of "trace" does not include the major contaminants of sulfur and chlorine, etc., although the simultaneous presence of such major species is always considered in our thermochemical calculations.

Of course, many other elements can vaporize in trace quantities from raw coal as either volatile, molecular compounds or as metallic vapors which, besides their deleterious action on the energy conversion systems, can also be detrimental to plant and animal life when emitted into the atmosphere. Hence, an understanding is sought of how the type and quantity of significant trace species in coal-gas changes from the coal pile through cleanup subsystems and the electric generators to the exhaust stack of an integrated system.

INTRODUCTION AND BACKGROUND

Behavior of coal contaminants toward potentially "very clean," highly efficient, integrated power generating systems, is becoming increasingly important from both a system's performance and endurance, as well as an environmental point of view. The overall project under this contract is entitled "TRACE ELEMENT EMISSIONS," and the goal is to investigate the fate and downstream effects of "trace" contaminant species during and after coal gasification.

The work has been performed in connection with the effects of trace elements on two advanced, coal gasifier with hot-cleanup, electric power generating technologies: viz., on Integrated Gasification Combined Cycle (IGCC) and on Integrated Gasifier Fuel Cell (IGFC) systems. A reasonably good understanding exists of the fate of major coal contaminants (i.e., sulfur, chlorine, alkali and nitrogen compounds) after coal combustion in steam-type power generating plants

with back-end cleanup. But only a limited amount of information exists concerning minor or trace contaminants and toxic species deriving from coal-gas, which may affect fuel cell and/or turbine systems. Attention is also paid to possible differences in 'toxic' emissions into the environment from these trace elements; especially in connection with integrated, substoichiometric, or mild gasification as compared to direct, high temperature, complete combustion of coal.

Thus the present study is a follow-on to several contaminant investigations at ERC (each time in cooperation with PSI-Technology Company) regarding the "Effects of Coal-derived Trace Species on Performance of Molten Carbonate Fuel Cells".¹ To implement the current study, ERC and PSIT again formed a team to respond to this research challenge with a side by side comparison of the two power conversion systems (i.e., a dual energy plant) consisting of one gasifier feeding two types of electric power generators. As shown in Figure 1, a variety of

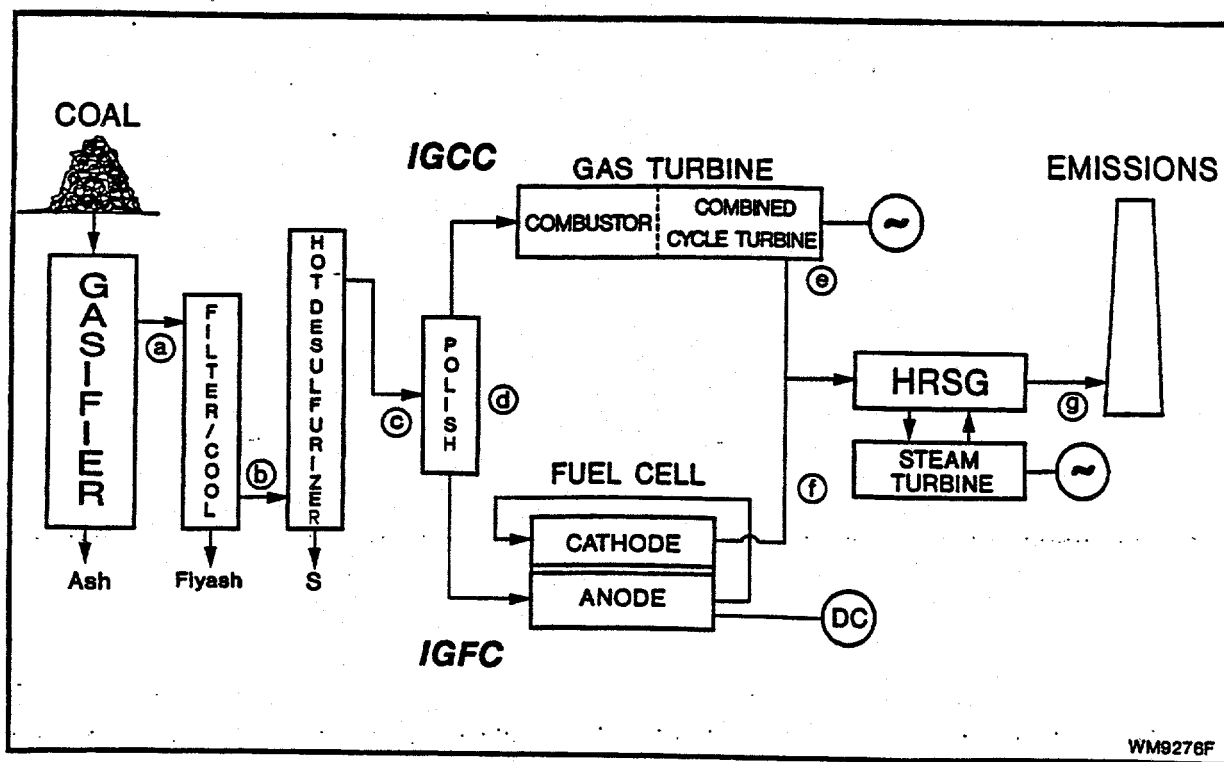


Figure 1. Integrated System Schematic For IGCC & IGFC Power Conversion Configuration for Comparison of the 2 Emerging Technologies as to Trace Element Effects.

node points between the gasifier and hot-cleanup subsystems and power convertors, were targeted as to the contaminant levels remaining at these locations. An understanding of what was required to achieve successful completion of this effort, such as technical expertise and past experience with the subject systems, as well as available equipment for simulating the relevant processes, was well represented by the two companies and the background² they possess in this area.

Selection of 5 Most Significant Trace Elements

Before the five trace elements that were to be studied in depth were selected, it was decided that a scoping experiment should determine the most significant elements being actually evaporated in typical coal gasification. Table 1 presents the information initially available in the form of an overview ranking contaminant elements by weighting factors (+) according to the

Table 1. Ranking of Coal Contaminants in Terms of Abundance, Volatility, and Toxicity
As, Se, Sb, Zn, and Pb, Were Selected as Most Significant Elements to be Studied.

ERC's Original Contaminant Ranking List showing gaseous concentrations (ppmv) in coal-gas if all species are vaporized as acid gases, halides, and metal vapors between 600° and 1000° C	UND-EERC ³ In Illinois #6 Solid Coal (wppm)		UND-EERC Highest Potential Vaporization of Elements into Coal- gas estimated from the solid coal data (ppmv)	Preliminary Ranking			
	1st sample	2nd sample		A B D U A N N C E	V O L L A I T T I Y	TOXICITY LISTS	
						EPA 17	DOE 11
<u>Majors</u>							
S 15,000	29,000	55,000	15,600	++++	+++		
Cl 500		470	120	++	+++	+	
Na 300		820	320	++	+++		
<u>Trace-metalloids</u>							
As 3.0	1.7		0.2	+	+++		+
Se 1.0	1.5		0.17	+	+++		+
Sb 0.1		< 1.0	0.07		++	+	+
<u>Trace-metals</u>							
Zn 100		65	9.0	++	+++		
Pb 3.0	3.2	6	0.26	+	++	+	+
Cd 0.2	0.14		0.011		+	+	+
Hg 0.01	0.032		0.0015		+	+	+
Cr 4	19	34	6.0	+		+	+
Ni 3	8.8	24	3.0	+		+	+
Mn 19				++			+
Be 2.3				+	?		+
<u>Additional</u>							
K		2200	512	++	+		
Co 1.5				+			+
Fe		23,000		+++			
<u>Generally Also Present</u>				Ti Al Si P Ca Mg Cu Ga Ge Mo Br			

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criteria of abundance in coal, volatility during gasification, and toxicity with respect to the environment. These early data have generally correlated quite well with subsequent gasification screening experiments, with Illinois #6 coal, that were done to definitively select arsenic (As), selenium (Se), antimony (Sb), zinc (Zn), and lead (Pb) as the five most significant elements to be studied in terms of coal-gas contaminant effects.

PROJECT DESCRIPTION

Thermochemical Calculations

The project was begun by conducting a literature search and developing the chemical properties data base for the different contaminant species that would be needed to compute site-specific thermodynamic equilibria of trace species interactions and possible condensed phase formation. Using this data base and the input from later gasification experiments which provided the types and concentrations of elements under initial gasifier exit conditions, theoretical trace species concentrations were calculated at various node points along the gas flow path from gasifier to power generating system. In this project, equilibrium modeling was conducted using a PC-based version of the SOLGASMIX computer code which minimizes the system free energy at certain locations (nodes) to predict the equilibrium phases - vapors, solids, liquids and condensed phase mixtures - as a function of local variables for complex multicomponent closed systems. In previous studies, the so-called SGM-CIS software was used to provide for calculation of 'Combined Ionic Solution' behavior as part of the SOLGASMIX program to especially account for sorption of trace species in the fuel cell's molten carbonate electrolyte.

Gasification Experiments

Experimental studies of the parameters of contaminant partitioning and distribution in coal-gas streams were begun with gasification studies performed at PSIT with Illinois #6 coal in a laminar flow, drop tube reactor, as shown in Figure 2, which was specially configured for ash classification and analysis. The unit was operated mostly by simulating conditions that occur in an oxygen-blown, Texaco gasifier, but were modified for ambient pressure application. Ash and flyash particles produced in these gasification runs were classified as to particle size distribution immediately after the reactor, and fractions separately analyzed for their elemental content by Neutron Activation Analysis (NAA) and Proton Induced X-ray Emission (PIXE).

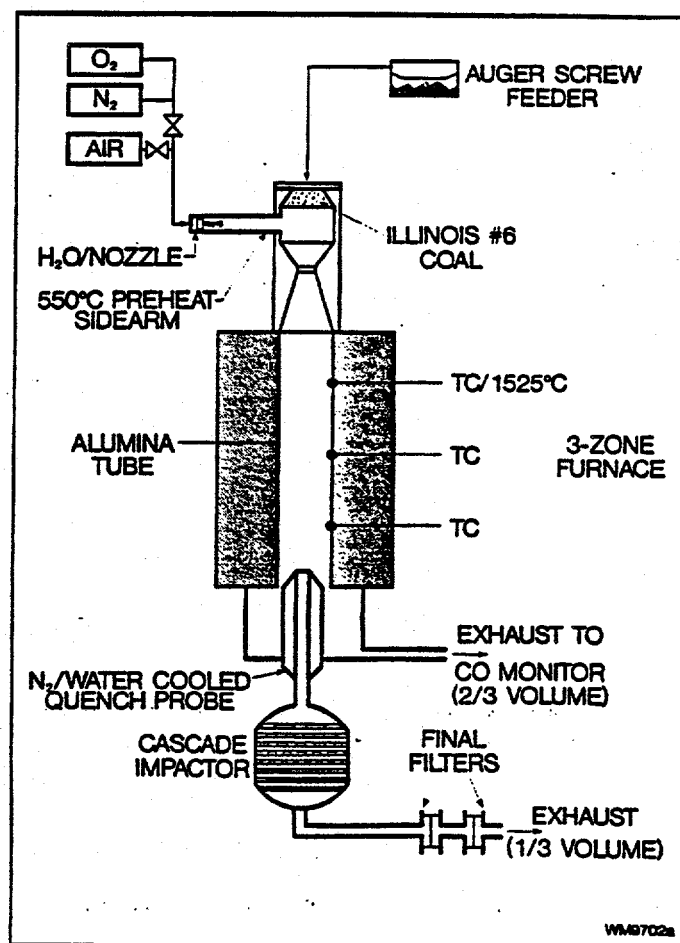


Figure 2. Laminar Flow, Drop Tube Reactor Configured for Ash Generation & Classification

Hence, volatile trace species sorption on both the ash particles produced in the reactor and trapped on the exit filters could be accurately studied for trace elemental content. Three types of gasification experiments were conducted. The first was an initial screening test to establish the five most significant volatile elements that were to be monitored in this work, and the second and third set of experiments were operated to further establish the effects of temperature, different oxygen levels, and hot ash filtration conditions on trace element partitioning.

Thermogravimetric Experiments

Numerous experiments to investigate desulfurization sorbents for their additional ability to also remove the 5 selected trace contaminants have been performed at ERC both in the past with

early types of Zn-based sorbents (ZnO and ZnFe_2O_4) and now with the latest most promising zinc titanate sorbent (ZT-4). In all these experiments there has been a concern that generically all zinc compounds, even though they may be made mechanically strong and regenerable, may at too high a temperature be thermodynamically unstable in reducing environment and eventually lose their active zinc constituent. These studies are now being further pursued in a Cahn, TG-131, thermogravimetric apparatus as shown in Figure 3. Studies of equilibrium sorption of the five most significant elements and their interaction species on ZT-4 are currently being performed at 500°C .

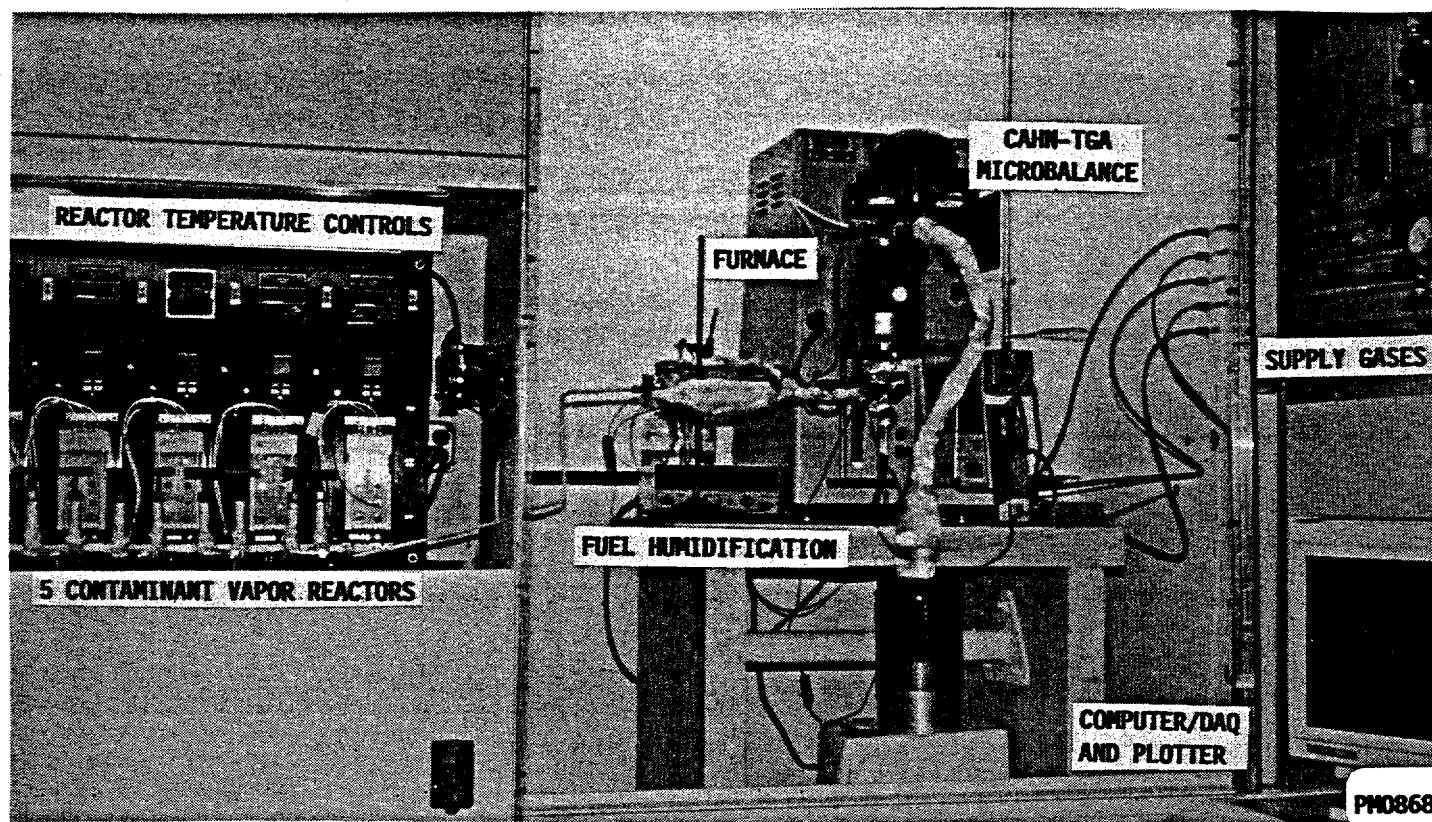


Figure 3. Thermogravimetric (TGA) Sorption Analysis Facility
Combinations of 5 Trace Elements Simultaneously, Plus H_2S and HCl , can be Handled.

Trace Element Capture Experiments

Prior work at PSIT has shown that aluminosilicates (perhaps as alkaline earth compounds) can react with several of the selected trace metals and metalloids at very high temperature (i.e., post-combustion) and in the presence of HCl and/or SO₂. The effectiveness of these sorbents is now being evaluated under conditions relevant to gasifier fuel conditions (i.e., in a strongly reducing environment) to be able to recommend useful, pre-combustion, control strategies. Trace species capture experiments with the five contaminants to be investigated are currently being performed by studying a number

of different materials in PSI's Trace Capture Reactor as shown in Figure 4. Low concentrations of trace contaminants are generated in this equipment in simulated coal-gas flow and immediately afterwards tested for absorption on various sorbents.

RESULTS & DATA

Thermodynamic Analysis

Because of the large variations in temperature, pressure, and gas composition throughout the IGCC and IGFC systems, the actual experimental determination of different amounts of each trace element, either neat or as binary interaction compounds, in gaseous or condensed form at the different node points, would have been prohibitively expensive. Therefore, as was also done in previous fuel cell studies, we have again resorted to thermochemical computation methods before performing the selective experiments representing an actual situation. Effects of the different variables on the partitioning of trace species among the different phases, including sorbent materials and other equipment components, can be quickly determined if the basic free energy data for all the species are available. For example, at 550°C and at 3 different pressures, computations were done for the high temperature incoming gaseous trace contaminant concentrations after node:b to become the lower temperature contaminant levels after node:c when the gas has been scrubbed in the presence of excess Zn₂TiO₄, as shown in Table 2. This clearly illustrates that merely by calculation very important conclusions can be quite rapidly drawn, such as the large amount of zinc that may be removed in the presence of HCl at the lower desulfurizer temperatures.

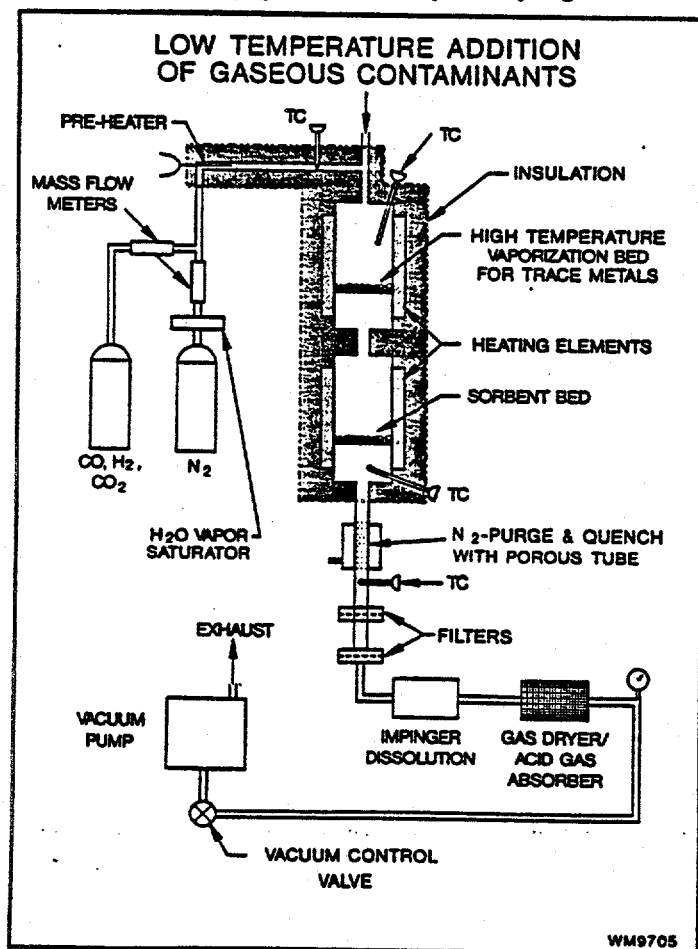


Figure 4. In-Line Element Capture Reactor Tests of Absorption of Generated Trace Species Can Be Rapidly Performed.

Table 2. Effects of Temperature, Pressure and Presence of Zn_2TiO_4 Sorbent on Gas Equilibria
Thermodynamic Calculation Provides Important Insights into 'Fate' of Trace Element Species.

Species	@ 827° before Sorbent Addition, Node:b			@ 550° C after Sorbent Addition, Node:c		
	1 atm	3 atm	10 atm	1 atm	3 atm	10 atm
As ₂	46.5	41.6	30.8	41.2	31.5	20.8
AsH ₃	5.6	15.6	40.1	12.3	18.8	24.8
As ₄	-	-	-	6.9	12.2	17.7
Sb	6.1	3.7	2.1	-	-	-
Sb ₂	11.7	13.0	14.1	7.0	4.6	2.8
Sb ₄	-	-	-	5.7	7.5	8.9
H ₂ Se	98.5	98.9	101.8	122.5	130.7	137.2
ZnSe	-	-	-	-	-	-
Zn	984.1	985.9	1005.7	247.2	46.3	7.5
ZnCl ₂	1.0	3.1	12.1	1077.8	993.1	951.7
ZnS	-	-	-	-	-	-
Pb	9.9	9.5	8.7	10.8	4.0	0.9
PbCl	1.0	1.7	2.9	38.4	31.0	18.1
PbCl ₂	-	-	-	24.0	43.0	60.9
PbS	48.1	48.2	49.3	0.3	0.2	0.1
% increase (decrease) in gas phase zinc before/after desulfurization due to presence of bulk Zn_2TiO_4				8%	(20%)	(30%)

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Gasification Testing

Knowing that inorganic contaminant elements and compound species present as vapors or as submicron-condensed particles, are extremely difficult to remove for analysis (from hot product gas) when using just cyclones, electrostatic precipitators, or even ceramic filter matrices, the approach taken was to combine several methods to provide gradual condensation, absorption, and (cold) submicron filtration to trap most of the trace element species vaporized from coal. During gasification, inorganic trace species will partition

as both vapors and as condensed phase species that become part of, or adsorbed on, the ash and flyash particles (e.g., mostly alumino-silicates) that are produced at the same time in a wide range of particle sizes. Thus, by simultaneously cooling and allowing the condensing trace species to adsorb on ash particles while also segregating the ash particles by size in a cascade impactor, it was possible to use this flyash as an analytical aid in identifying the time/temperature histories (and therefore volatility) of many of the trace element species that are of interest both qualitatively and quantitatively.

As shown in Table 3, once species were segregated on the 7 cascade impactor stages (representing d_{50} particle ranges of $10\mu\text{m}$ down to $<0.3\mu\text{m}$) and then on 2 submicron filters, it was clearly evident which elements were not present as

volatile species (e.g., Fe, Ni, Mn, Cr, etc) and which had remained volatile toward the end until being adsorbed at the lowest temperature finest filtration stages (e.g., As, Se, Sb, Zn and Pb).

Table 3. Composite NAA and PIXE (wppm) Data of Filter and Impactor Stage Ash Analysis
Combined Data from 8 Experimental Runs Have Elucidated Relative Trace Element Volatilities.

ELEMENTS	Cascade Impactor Stages, wppm				Polycarbonate Filter wppm	Final Filter Activated Carbon
	1	3	5	7		
<u>Majors</u>						
S	1900	-	-	1900	37,000	-
Br	120	2	11	~16	1240	0
Na	2700	4700	-	0	~400	0
K	7500	-	1500	66	1600	-
<u>Minors</u>						
As	2	5	-	11	28	0
Se	3	6	-	9	~51	0
Sb	-	1	-	4	12	0
<u>Trace Metals</u>						
Zn	~130	450	1300	~785	~5600	17,000
Pb	-	-	250	300	2500	-
Cd	1	2	-	1	2	-
Hg	-	1	-	1	1	2000
<u>Metals</u>						
Ni	590	-	140	95	140	-
Fe	~71,000	~61,000	19,000	~570	~1200	0
Mn	350	-	100	4.4	-	-
Cr	~765	430	280	~24	52	0

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TGA - Runs

The concern in our TGA-sorption experiments with regard to baseline stability of sorbent material before introducing the various trace element species, has led to several initial runs with H_2 , 20% humidified H_2 , and with simulated coal-gas of a nominal composition (i.e., 26% H_2 , 38% CO , 25% H_2O , 9% CO_2). Alternating temperature ramping ($50^\circ C$ steps starting at $400^\circ C$) and isothermal equilibration periods of ~ 12 hours, were used to investigate the baseline stability of zinc titanate, as shown in Figure 5. A susceptor with titanate sorbent evenly distributed in 5 levels or pans (average of ~ 1.2

gram per pan), was used to follow the weight changes of the sorbent material for total run periods of up to 72 hours. It is seen that at the max. $500^\circ C$ temperature, the material remains sufficiently stable to follow low level weight increases that we expect to observe in connection with trace species absorption of a number of trace elements on this sorbent. These runs are currently in progress.

Trace Element Capture Testing

Tests are in progress but insufficient data are available at this time.

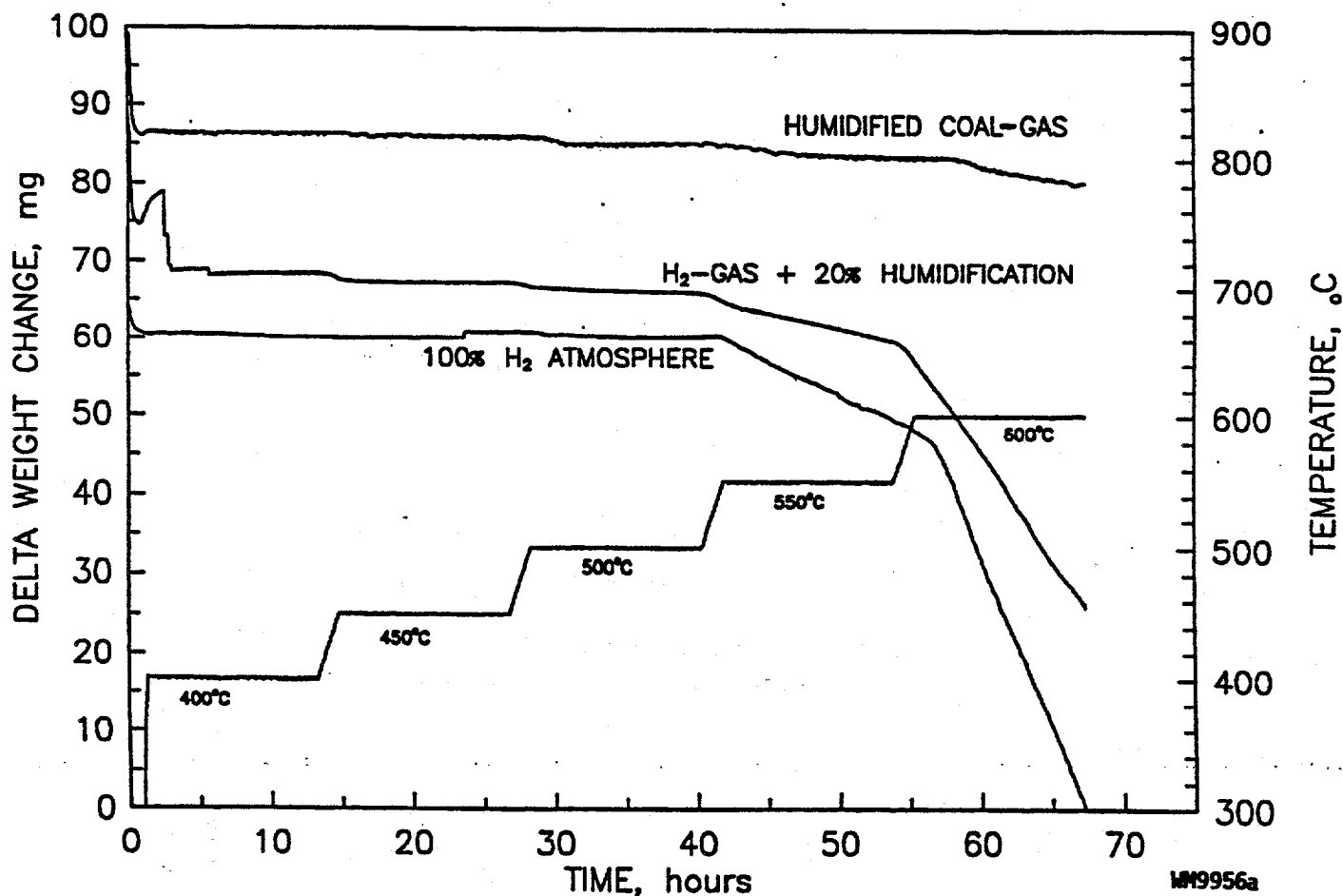


Figure 5. TGA Experimental Runs with (~ 6 gram) Samples of Sorbent
Examination of Effects of Temperature and Humidity on Stability of Zn_2TiO_4 in Reducing Atmosphere for Trace Element Sorption Studies.

FUTURE WORK

To sum up this present investigation of the 'fate' of contaminants at various sites that are of concern to evolving integrated power systems, it is seen that the five most significant trace elements generated by coal gasification, have been identified. And also, that a pattern for their control and removal at high temperature is evolving. However, since only limited theoretical calculations were done within the scope of the current program and experimental con-firmations are also needed, there are still a number of areas where future work in a follow-on program is recommended. For example:

Thermochemical Calculations

The power of our computer research technique has become well established and together with additional modeling would further advance the general ability to quickly predict trace element behavior and effects on IGCC and IGFC systems.

Three specific areas requiring calculational effort are at: 1) *The Gasifier*. Formation of complex aluminosilicates with the 5 trace elements, and correlation with experimental partitioning data as a function of existing gasification conditions. Clearly, the ability to develop a model that better defines aluminosilicate formation from different coals, and which is gasification conditions specific, would be of great use to tailor the type of gasifier and operating conditions needed for optimum integration into power conversion systems; 2) *Hot-Gas Cleanup*. Interaction of trace elements with other than zinc titanate desulfurization sorbents should be considered. Modeling of contaminant interactions with zinc titanate sorbents using equilibrium thermochemistry has been successful. Similar calculations should now be done for other sorbents to determine the utility of a variety of likely desulfurization materials that could also be

beneficial for trace contaminant or metal vapor removal; 3) *NiO-cathode on O₂-rich side of Matrix*. Interactions of trace elements in this part of the carbonate fuel cell, after anode exit-gas is recycled (and oxidized for CO₂ recovery) and trace species become reexposed to the molten carbonate electrolyte, are still a concern that has not yet been addressed.

Gasification Experiments

In our current program, the concentration of trace elements as a function of ash particle size sorption was measured primarily for volatility determination. Only limited experiments were conducted to start assessing the effects of gasification conditions and temperature on changes in trace element volatilization. Results indicate that trace element vaporization is dependent on gasifier stoichiometric conditions, where the amount of an element vaporizing decreases with increasing partial pressure of oxygen in the system; this also increases the ash particle temperature. To explore this interaction in more detail and to determine whether gasification conditions can be optimized to improve trace element capture, a detailed study examining trace element partitioning as a function of gasification stoichiometry, pressure, and other parameters, should be considered.

Thermogravimetric Experiments

Initial equilibrium experiments of weight loss or gain should usually be considered as a preliminary test in determining a sorbent's stability and its affinity for removing low level gaseous trace species, which can then serve to confirm whatever the thermochemical calculations may have indicated. These TGA-runs can be very simply and rapidly performed, and can also be used to establish the regenerability of materials in different gas atmospheres. Such runs are currently being performed at ERC in connection with a new material and a method for trace element polishing.

Trace Element Capture Experiments

In-line experiments which can closely simulate high temperature contaminant absorption conditions, can elucidate the kinetics of immediate (post-gasification) trace element capture using a variety of materials. Studies of activated sorbents for early removal of the five significant elements are now employing this methodology. In this respect, it is also recommended to expand the test matrix to study early capture of additional elements such as chlorine, cadmium, and mercury species. Another area would be to combine activated sorbents with zinc-based, hot-gas desulfurization (in a single or dual bed reactor) and evaluate the combined effect of also removing trace elements together with sulfur.

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